

# Electrochemical CO<sub>2</sub> reduction reaction on **cost-effective oxide-derived copper** and **transition metal-nitrogen-carbon** catalysts

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## Abstract

The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) either to generate multi-carbon (C<sub>2+</sub>) or single carbon (C<sub>1</sub>) value-added products provides an effective and promising approach to mitigate the high CO<sub>2</sub> concentration in the atmosphere and promote energy storage. However, cost-effectiveness of catalytic materials limits practical application of this technology in the short term. Herein, we summarize and discuss recent and advanced works on cost-effective oxide-derived copper (OD-Cu) catalysts for the generation of C<sub>2+</sub> products (hydrocarbons and alcohols) and transition metal-nitrogen-doped carbon (M-N-C) electrocatalytic materials for C<sub>1</sub> compounds production from CO<sub>2</sub>RR. We think they represent suitable electrocatalyst candidates for scaling up electrochemical CO<sub>2</sub> conversion. This short review may provide inspiration for the future design and development of innovative active, cost-effective, selective and stable electrocatalysts with improved properties for either the production of C<sub>2+</sub> (alcohols, hydrocarbons) or carbon monoxide from CO<sub>2</sub>RR.

## Keywords:

Carbon dioxide electrochemical reduction reaction; Electrocatalysis; Oxide-derived copper catalysts; Transition metal-nitrogen-carbon catalysts; Value-added products

## Introduction

The greenhouse gas carbon dioxide ( $\text{CO}_2$ ) concentration in the atmosphere is sustainably increasing, leading to a monthly averaged value of 411.76 ppm recently, thus causing severe environmental impacts and energy issues.[1,2] Among the available  $\text{CO}_2$  mitigation approaches, carbon capture and storage (CCS) and carbon capture and utilization (CCU) strategies are currently under development with the purpose of closing the anthropogenic  $\text{CO}_2$  cycle [3–5]. The development of materials for efficient  $\text{CO}_2$  capture is essential to facilitate a closed carbon cycle, nevertheless the focus of this article is on available technologies for converting  $\text{CO}_2$  into value-added products.[6–9] In particular, electrochemical  $\text{CO}_2$  reduction reaction ( $\text{CO}_2\text{RR}$ ), which is powered by electricity, has attracted the scientific community attention for producing different fuel feedstocks such as carbon monoxide ( $\text{CO}$ ) [10,11], formic acid ( $\text{HCOOH}$ ) [12–14], methane ( $\text{CH}_4$ ) [15,16], methanol ( $\text{CH}_3\text{OH}$ ) [17,18], ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) [19,20] and ethylene ( $\text{C}_2\text{H}_4$ ) [21,22], etc.  $\text{CO}_2\text{RR}$  is mainly studied in aqueous media, however organic solvents and ionic liquids have also been explored.[23–25] The selectivity of this reaction is affected by different factors, such as the properties of both cathode electrocatalytic material and electrolyte, as well as the potential applied.[26–29] Moreover, another important aspect is the cell/electrolyzer design effect on productivity, selectivity and energy efficiency of  $\text{CO}_2\text{RR}$ . The simple undivided cell configuration has been replaced by two-compartment electrolyzers to avoid the reoxidation of reduced species. In addition to this, vapor-fed systems using gas diffusion electrode (GDE) and membrane electrode assembly (MEA or zero-gap assembly) configurations have been proposed to improve the transport of  $\text{CO}_2$  to the catalyst surface, eliminating ohmic losses and thus maximizing energy efficiency [30,31].

Nowadays, efficient electrocatalytic materials with high electrocatalysis, strong stability and high product selectivity must be explored with the purpose of lowering the high overpotential of  $\text{CO}_2\text{RR}$ , avoiding also the effect of the competitive hydrogen evolution reaction (HER), which negatively affect the selectivity of the reaction toward the target product. In this context, different metallic

electrocatalysts have been studied for CO<sub>2</sub>RR, ranging from Cu (it seems to be the unique metal selective for hydrocarbons and alcohols formation) [32,33] to Au, Ag, Zn (mainly producing CO)[34–36] and Pb, In, Sn, Bi (formate/formic acid generation).[13,37–39] Nonetheless, there are still many challenges to be addressed to reduce the overpotential and control the selectivity of CO<sub>2</sub>RR on metallic electrocatalysts [40]. The main key parameters that need to be studied to improve both activity and selectivity are, among others, operating conditions (applied voltage, current density, catalyst loading, etc.) [41], electrolyte type and its concentration [26,42], local pH [43] and particle size [44].

From an industrial implementation point of view, generation of multi-carbon (C<sub>2+</sub>) products (hydrocarbons and alcohols) from CO<sub>2</sub>RR at Cu-based electrocatalysts represents an appealing approach because of their high energy density (used as liquid fuels) compared to C<sub>1</sub> feedstocks.[28,45] Nevertheless, Cu atoms mobility during CO<sub>2</sub>RR (especially in the presence of CO) is well-known and provokes surface restructuring, which affects the electrode activity and product selectivity. For this reason, oxide-derived copper (OD-Cu) electrocatalytic materials have been widely studied in recent years, since OD-Cu electrodes provide better long-term stability under reaction conditions and keep a similar product selectivity [46]. Oxidation pretreatments on Cu electrodes can either increase surface roughness or provide subsurface oxygen at the electrocatalyst surface, which may lead to improve CO<sub>2</sub>RR performance.[47–49]

Additionally, another interesting cost effective approach based on pyrolyzed catalysts for C<sub>1</sub> compounds production from CO<sub>2</sub>RR, is reviewed in this work. In particular, transition metal-nitrogen-doped carbon (M-N-C) materials have been already studied for CO<sub>2</sub>RR[50,51], HER[52] and Oxygen Reduction Reaction (ORR)[53,54] because of their high selectivity, stability and activity, huge catalytic surface area and low-cost. So far, generation of C<sub>2+</sub> products from CO<sub>2</sub>RR is not possible on M-N-C catalysts, since those are considered single active site catalysts and do not allow carbon-carbon coupling. Since Varela et al. reported the utilization of Fe/Mn-N-C for the first time on CO<sub>2</sub>RR to CO with a Faradaic efficiency (FE) of 80% in 2015[55], there have been several attempts to explore different metals in M-N-C to catalyze CO<sub>2</sub>RR such as Fe, Co, Ni, Mn, Cu, Cr, etc.[52,56,57] Among all these metals, Fe-N-C and Ni-N-C exhibit superior electrocatalysis by lowering the overpotential and improving CO selectivity, respectively.[56,58] Each component in

M-N-C catalysts for CO<sub>2</sub>RR may have a particular impact on the overall activity performance, since different types of carbon, nitrogen source and metallic center have been explored.[59–61] However, most of the studies for CO<sub>2</sub>RR have been mainly focused on the effect of different metallic centers in M-N-C catalysts.

To sum up, this work is mainly focused on the product-selectivity performance for CO<sub>2</sub>RR on two types of cost-effective electrode materials, since we think they are feasible electrocatalytic material for real applications: i) OD-Cu catalysts for C<sub>2+</sub> products formation, and ii) M-N-C materials for C<sub>1</sub> compounds production.

### **OD-Cu catalysts for multi-carbon products generation (alcohols and hydrocarbons)**

Copper seems to be the unique metal which shows in literature the possibility of converting CO<sub>2</sub> into multi-carbon products (i.e. C<sub>2+</sub> alcohols and hydrocarbons) with significant efficiencies.[62] Nevertheless, several drawbacks such as catalyst activity decrease during electrolysis and product selectivity limit the practical application of this technology in the short term. Different electrochemical and non-electrochemical oxidation pretreatments on Cu electrodes have been already tested to synthesize OD-Cu materials, since a relevant increase in grain boundaries and a rougher surface is created on those OD-Cu electrodes as soon as the required potential for CO<sub>2</sub>RR is applied [63]. However, alterations in catalyst structure and morphology during CO<sub>2</sub>RR may negatively affect the productivity and selectivity. Deactivation is mainly attributed to catalyst physical detachment due to HER, surface poisoning by adsorption of CO<sub>2</sub>RR intermediates and/or restructuring of the electrode surface under reaction conditions.[64,65] This is not usually relevant when high surface area OD-Cu electrodes are used, otherwise it is an issue that must be addressed. In this regard, the continuous investigation on the CO reduction reaction mechanism, which is a key intermediate reaction to produce C<sub>2+</sub> hydrocarbons and C<sub>2+</sub> oxygenated products should help to move forward the development of alternative electrocatalysts and optimize operating conditions for CO<sub>2</sub>RR. Furthermore, OD-Cu electrocatalytic materials selectivity for CO<sub>2</sub>RR can also be tuned by the electrolyte. In particular by controlling the buffer capacity, local pH, anion and cation of the supporting electrolyte in solution [26,42,43]. Neutral unbuffered and alkaline aqueous solutions favor formation of C<sub>2+</sub> over C<sub>1</sub> products on OD-Cu electrodes. For this reason, oxidation-reduction cycles at the OD-Cu electrodes, which create a higher roughness

electrode surface, lead to a higher local pH close to the electrode surface, which enhances  $C_{2+}$  products formation. Additionally, electrolyte anions and cations play a critical role in the  $CO_2RR$  selectivity towards  $C_{2+}$  products, being  $CS^+$  as alkali cation and halides as anions the most active electrolytes for that purpose.

Herein, we summarize recent research on OD-Cu electrocatalysts with high catalytic efficiency and activity (Table 1). Since Frese et al. firstly reported that OD-Cu electrodes can be used to convert  $CO_2$  to methanol in aqueous solution, [66] several authors have extensively investigated the use of OD-Cu surfaces in  $CO_2RR$  for alcohols production. For instance, the treatment of  $Cu_2O$  with Prussian Blue analogue (K-PBA) to form core-shell nanocubes ( $Cu_2O@K-PBA$ ) increases  $C_{2+}$  products yields with FE of 23.9% (ethylene 10.8%, ethanol 3.6% and n-propanol 9.5%) due to the ability of K-PBA for changing the intrinsic energetics of  $Cu_2O$ . [67] From another point of view, theoretical methods such as the density functional theory (DFT) may provide a new approach to study reaction mechanisms of  $CO_2RR$ -to-methanol process on  $Cu_2O$ . [68] Thus, DFT was used to investigate the formation of the helpful reaction intermediate  $CH_3OH^*-OH^*$ , as well as figuring out the influence of catalyst surface morphology and solvation during methanol formation from  $CO_2RR$ . Furthermore, the authors also strengthened the “variation trend of charge distribution”, leading to the choice of “minimum-energy pathway”.

Likewise, a lot of efforts have been also dedicated to develop and improve OD-Cu electrocatalysts for  $CO_2RR$  to produce  $C_{2+}$  hydrocarbons. For instance, Boron-doped OD-Cu greatly catalyze  $CO_2$  to  $C_2$  products owing to the impact of Boron on stabilizing  $Cu^+$  species. [69] In this regard, the effect of Zn on stabilizing  $Cu^+$  atoms as well as suppressing  $H_2$  evolution in Cu oxides/ $ZnO$ -based electrocatalytic surfaces for the production of hydrocarbons from  $CO_2RR$  was also illustrated, leading to an outstanding performance toward ethylene with FE as high as 91.1%, which the authors associated to the synergic effect between Cu oxides and  $ZnO$ , with improved adsorption of reaction intermediates for the generation of ethylene. [70] Similarly, N-doped carbon ( $N_xC$ ) was adopted as a carrier of  $CuO$  by catching more  $CO_2$  to increase ethylene selectivity. Compared to  $CuO$  loaded onto carbon black, the former shows better ethylene selectivity and activity. This research provides an efficient method to increase catalytic activity and reaction selectivity by combining  $CuO$  and  $CO_2$  capture materials. [71] In addition, the utilization of ionic liquid functionalized graphite sheets was also studied for controlling the

morphology and size of Cu<sub>2</sub>O nanocubes (Cu<sub>2</sub>O/ILGS).[72] Cu<sub>2</sub>O/ILGS are able to inhibit the latter's aggregation, thus enlarging the surface active sites for CO<sub>2</sub>RR and reaching a high ethylene efficiency (Fig 1a). Moreover, OD-Cu catalysts may modify their morphology during CO<sub>2</sub>RR. For example, Cu<sub>2</sub>O nanoparticles can undergo fragmentation to smaller pieces during the electrochemical process, thus increasing compact morphology and grain boundaries, which may facilitate the selectivity and activity toward C<sub>2+</sub> products.[73] Fig.1b shows a typical OD-Cu electrode morphology with numerous grain boundaries. In particular, grain boundaries play a crucial role for faster oxygen diffusion and oxide nucleation in OD-Cu catalyst. The high presence of grain boundaries in the catalyst structure is responsible for promoting the formation of C<sub>2</sub>/C<sub>3</sub> products.[74][75] Interestingly, the major impact of applied potential and current on reaction selectivity at OD-Cu catalysts was proven.[76] The authors prepared 3 different kinds of OD-Cu films with different surface roughness factors and illustrated that product selectivity relies on surface roughness: methane, ethylene, ethanol, CO or formate generation can be improved successively as the OD-Cu films surface roughness aggravates. As shown in Fig. 1c, 1d and 1e, the control of the applied potential (ranging from -0.45V to -1.3 V vs. RHE) is crucial to tailor the selectivity of CO<sub>2</sub>RR. The different products are related to the different energy barriers in the CO<sub>2</sub>RR process. For instance, a slightly rough metallic Cu surface (Cu-10) produces preferentially CH<sub>4</sub> while OD-Cu surfaces (CuO-1, CuO-10 and CuO-60) produce more C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH. In addition to this, the method of isotopic labelling, which can trace the products composition and uncover the reaction mechanism by supplying isotopic reactant, provides information to understand product distribution during CO<sub>2</sub>RR. This method can be used for the correct identification of active sites in electrocatalysis, that is, the specific facet/feature on the catalyst surface where CO<sub>2</sub>RR to form the target product is taken place.[77] For instance, given a mixture of <sup>13</sup>CO and <sup>12</sup>CO<sub>2</sub>, three different existing active sites were identified for different C-C coupled products formation from CO<sub>2</sub>RR at OD-Cu catalysts such as ethylene, ethanol/acetate and 1-propanol, respectively.

### Transition Metal-Nitrogen-Carbon materials for single carbon products generation

As mentioned above, OD-Cu materials mainly boost the catalytic activity for promoting the formation of C<sub>2+</sub> products. For CO generation, however, M-N-C catalysts (Fig. 2a) have been widely studied in literature due to their numerous active sites of synergistic M-N<sub>x</sub> moieties on their huge surface area, which might modify the binding energy of key reaction intermediates related to CO<sub>2</sub>RR. Unfortunately,

these transition metals have excellent and prior catalysis on competing side HER rather than CO<sub>2</sub>RR. However, when metal arrangement goes into a single atom structure, its electrocatalytic role on CO<sub>2</sub>RR can be greatly enhanced due to the electronic environment, which has received a lot of attention recently.[60] The comparison of CO faradaic efficiencies (FEs) at different metals-N-C electrocatalysts as a function of the applied potential is shown in Fig.2b. The highest CO production efficiency is exhibited by Ni-N-C, but the lowest overpotential is achieved by Fe-N-C catalyst. For these reasons, we focus this section in Fe-N-C and Ni-N-C catalysts for CO<sub>2</sub>RR. The identification of single active sites on those catalyst depends on each case, since the nature of the metal center and its coordination environment define different types of active sites (M-N, M-C, M-N<sub>2+2</sub>, M-N<sub>4</sub>-C...), which mainly control activity and selectivity in M-N-C catalysts.[50] For instance, the utilization of porous nanosphere Fe-N-C for CO<sub>2</sub>RR to CO shows an interesting high FE (around 90%), where the key aspect in terms of active sites was demonstrated to be the synergistic role between the single-atom Fe-N<sub>4</sub> moieties and adjacent C [78]. In addition, rotating disk electrode (RDE) was used to carry out linear sweep voltammetry (LSV) analyses in order to measure the electrochemical response in the presence or absence of Fe center (Fig.2c). In this regard, the presence of Fe center notably enhances the catalytic performance despite nitrogen moieties are already catalytically active for CO<sub>2</sub>RR. This leads to the conclusion that the Fe atom plays a vital role in the active sites of the electrocatalytic material for an efficient CO<sub>2</sub>RR. In this context, DFT calculations were used to evaluate the nature of real active sites in this type of electrocatalyst. It was proven that the most active sites are the Fe-N<sub>4</sub> moieties surrounded by defective graphitic carbon, because this kind of moieties possesses the smallest Gibbs free energy (Fig.2d). Surprisingly, this research reports an extremely small overpotential of 90 mV, which is the lowest reported for Fe-N-C catalysts.[79]. Zhou et al. stated that Fe-N-C materials derived from Fe(SCN)<sub>3</sub> (denoted as SMFeSCN) are responsible for an improved FE to CO up to 99% at a moderate overpotential of 0.44 V, in comparison with the performance reached on SMFe (without SCN). Nevertheless, this enhancement was mainly attributed to the 3D graphene microporous nanostructure of SMFeSCN, which leads to an increased CO<sub>2</sub> local concentration.[80] Another strategy following this approach is based on sulfur (S) incorporation in the Fe-N-C synthesis for producing numerous micropores and high surface area electrodes, which reach an enhanced FE for CO generation of 98%.[81] The dopant S is embedded in the graphitic layer together with Fe-N<sub>4</sub>, thus



increasing the activity of the latter by changing its Fermi level and charge density (Fig.2e and 2f).unlike Fe-N-C catalysts, which are beneficial for lowering the overpotential for CO formation, Ni-N-C materials are popular mainly because of their high CO selectivity. This fact is mainly attributed to the presence of Ni single atoms within the Ni-N-C electrocatalysts.[60] Based on this, we summarize here the proposed active sites present on those catalysts, which justify high FEs to CO achieved on Ni-N-C electrocatalysts. The combination of experimental and DFT calculations proved that N and C surrounding Ni atoms can help the transportation of electrons through Ni d orbital to reactants and lower the energy [82]. In principal, the most important active sites are located in the Ni-N<sub>x</sub> moieties, which can act either in a synergistic way with different N or be affected by the surrounding environment. For instance, two different groups of research have demonstrated the importance of pyrrolic N in the synergistic effect with Ni-N<sub>x</sub> by controlling nitrogen precursors in an attempt to tune the catalytic activity for FEs of 96.5% and 80% to CO, respectively. [83] [84] In addition to this, different Ni-N<sub>x</sub> moieties can be found depending on the number and species of N and the surrounding environment, causing different catalytic activities. As a result, DFT is used to analyze the most valuable active site Ni-N<sub>x</sub>. [85,86] In this regard, the free energies of the intermediate \*COOH on different Ni-N-doped carbon nanotubes such as Ni@N<sub>3</sub> (pyrrolic), Ni@N<sub>3</sub> (pyridinic) and Ni@N<sub>4</sub>, respectively, were calculated [85]. Ni@N<sub>3</sub> (pyrrolic) was the most efficient active site due to its lowest free energy (Fig. 3a). Moreover, rhombic dodecahedron shape of Ni-N-C was also developed in order to compare the behavior of this catalysts in the presence/absence of the metal center (Ni). Thus, Ni-N-C showed better electrocatalysis than N-C catalyst in terms of high FE toward CO (Fig.3b) and more positive onset potential (Fig.3c). Nevertheless, the authors found out that Ni-N<sub>4</sub> (Ni-N<sub>4</sub>-C<sub>10</sub>) matters in the catalysis reaction, that is, in other words, the edge-located Ni-N<sub>2+2</sub> (Ni-N<sub>2+2</sub>-C<sub>8</sub>) is responsible for the high selectivity to CO (96% FE) rather than Ni-N<sub>4</sub> in bulk Ni-N-C rhombic dodecahedron (Fig.3d).[86] These conclusions may provide new insights into the synthesis of specific Ni-N-C electrocatalysts with desired properties for an improved CO<sub>2</sub>RR-to-CO process efficiency and selectivity. In conclusion, M-N-C catalysts are promising low-cost catalytic materials for CO generation from CO<sub>2</sub>RR due to their enhanced electrocatalytic activity compared to metal-free N-doped carbon materials, especially Fe-N-C and Ni-N-C catalysts, which shown excellent performance for converting CO<sub>2</sub> to CO with high FEs.



## Conclusions

In summary, the most recent trends on cost-effective OD-Cu catalysts and M-N-C materials for the CO<sub>2</sub>RR in aqueous media are reviewed here. On the one hand, different operating conditions (pH, electrolyte, applied potential etc.) as well as electrode morphology control and increased surface roughness seem to dramatically enhance the performance of CO<sub>2</sub>RR to C<sub>2+</sub> products (alcohols and hydrocarbons) in terms of reaction selectivity and catalyst activity. In our opinion, most of the future research on OD-Cu catalysts should be focused on continuing the study of the CO reduction reaction mechanism, which is a key intermediate reaction to produce C<sub>2+</sub> hydrocarbons and C<sub>2+</sub> oxygenated products on OD-Cu catalysts. On the other hand, pyrolyzed catalysts for C<sub>1</sub> compounds production (mainly CO) such as Fe-N-C and Ni-N-C materials have already demonstrated an outstanding FE to convert CO<sub>2</sub> into CO at low overpotentials. Some controversy is present in the identification of the real active sites on those materials. Most of the reported studies agree in the nature of the metal center and its coordination environment with the surrounding nitrogen and carbon atoms as the main active sites. Nevertheless, the long-term stability of M-N-C materials is still an issue, since relevant leaching of the metal center is produced under reaction conditions during CO<sub>2</sub>RR. For this reason, we suggest to concentrate future research developments on that. Finally, this short review may provide new insights for the future development of cost-effective, selective, and stable electrocatalysts for an improved CO<sub>2</sub>RR performance toward the generation of different types of value-added products.

## Conflict of interest statement

The authors declare no interest conflict.

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Table 1. Comparison of the performance of different OD-Cu catalysts recently reported in literature for CO<sub>2</sub>RR.

Fig. 1 (a) Schematic presentation of CO<sub>2</sub> electroreduction to C<sub>2</sub>H<sub>4</sub> on interface-induced method to prepare Cu<sub>2</sub>O nanocubes on ionic liquid functionalized graphite sheets. Reprinted with permission from ref [72]. Copyright 2019 Elsevier. (b) HRTEM image for Cu based nanoparticles after 10 h of CO<sub>2</sub>RR. Adapted with permission from ref [73]. Copyright 2019 American Chemical Society. (c) (d) (e) Faradaic efficiency of methane, ethylene and ethanol, carbon monoxide and formate on different catalysts at different potentials, respectively. Different catalysts Cu-10, CuO-1, CuO-10, and CuO-60 are Cu based catalysts electrodeposited for 1 min, 10 min and 60 min, respectively, which are shown in color of orange, green, red and blue, respectively. Error bars in (c)–(e) represent the standard deviations of three independent measurements. Open access article ref [76]. Distributed under the terms of the Creative Commons CC BY license.

Fig. 2 (a) General synthesis strategy of M-N-C catalysts and their obtained structure. Reprinted with permission from ref [50]. Copyright 2019 American Chemical Society. (b) CO FEs at different metal-N-C catalysts. Reprinted with permission from ref [56]. Copyright 2018 Elsevier. (c) LSV curves of Fe–N–PC, op–Fe–N–PC and N–PC in CO<sub>2</sub>-saturated 0.5 mol·L<sup>-1</sup> KHCO<sub>3</sub> solution (scan rate = 10 mV/s). Reprinted with permission from ref [78]. Copyright 2019 American Chemical Society. (d) Gibbs free energy diagrams of CO<sub>2</sub>RR on different sites by DFT. Reprinted with permission from ref [79]. Copyright 2019 American Chemical Society (e) S doped Fe-M-C structure. (f) Comparison of FEs to CO in 0.1 M KHCO<sub>3</sub> aqueous solution on different catalysts. Reprinted with permission from ref [81]. Copyright 2019 Elsevier.

Fig.3 (a) Free energy diagram of CO<sub>2</sub>RR to CO on Ni@N<sub>4</sub>, Ni@N<sub>3</sub> (pyrrolic) and Ni@N<sub>3</sub> (pyridinic). Reprinted with permission from ref [85]. Copyright 2019 John Wiley and Sons. (b) CO and H<sub>2</sub> Faradaic efficiency and (c) CO partial current density for N–C and Ni–N–C. (d) Initial and final states for the COOH dissociation reaction on Ni–N<sub>4</sub>–C<sub>10</sub> and Ni–N<sub>2+2</sub>–C<sub>8</sub> sites. Reprinted with permission from ref [86]. Copyright 2019 Royal Society of Chemistry.

Table 1.

OD-Cu catalysts	Electrolyte	E / V vs. RHE	Target products	FE (%)	Ref
Cu <sub>2</sub> O NP	KHCO <sub>3</sub>	-2.0 V vs. SHE	CH <sub>3</sub> OH	47.5	[17]
Cu <sub>2</sub> O@K-PBA	n.a.	-1.11	C <sub>2</sub> H <sub>4</sub>	23.9	[67]
B-OD Cu	0.1 M KHCO <sub>3</sub>	-1.05	C <sub>2</sub>	48.2	[69]
Cu oxides/ZnO	0.1 M KHCO <sub>3</sub>	-2.5 V vs. Ag/AgCl	C <sub>2</sub> H <sub>4</sub>	91.1	[70]
CuO/N <sub>x</sub> C	0.1 M NaHCO <sub>3</sub>	-1.25	C <sub>2</sub> H <sub>4</sub>	36	[71]
Cu <sub>2</sub> O/ILGS	0.1 M KHCO <sub>3</sub>	-1.15	C <sub>2</sub> H <sub>4</sub>	31.1	[72]
Cu <sub>2</sub> O NP/C	0.1 M KHCO <sub>3</sub>	-1.1	C <sub>2</sub> /C <sub>3</sub>	74	[73]
OD Cu	0.1 M KHCO <sub>3</sub>	-1.0	C <sub>2</sub> /C <sub>3</sub>	60	[74]
Cu <sub>x</sub> O	2.0 M KOH	-1.17	C <sub>2</sub>	40	[75]
Different OD Cu	0.1 M KHCO <sub>3</sub>	-0.9 ~ -1.1	C <sub>2</sub>	48	[76]
		-1.15	CH <sub>4</sub>	40	
		-0.5	CO	46	
		-0.6	HCOO <sup>-</sup>	35	

Abbreviations: Nanoparticles (NP), Prussian Blue Analogue (PBA), B-OD (Boron-doped oxide-derived) and Ionic Liquid functionalized Graphite Sheets (ILGS).

Fig.1

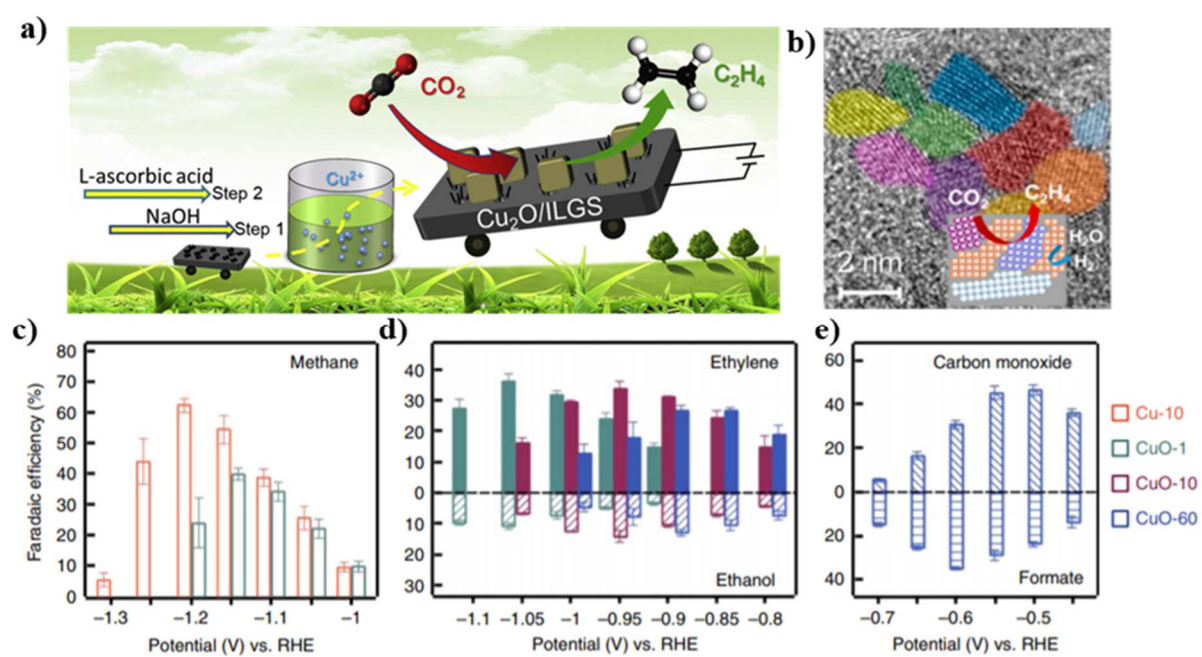




Fig.2.

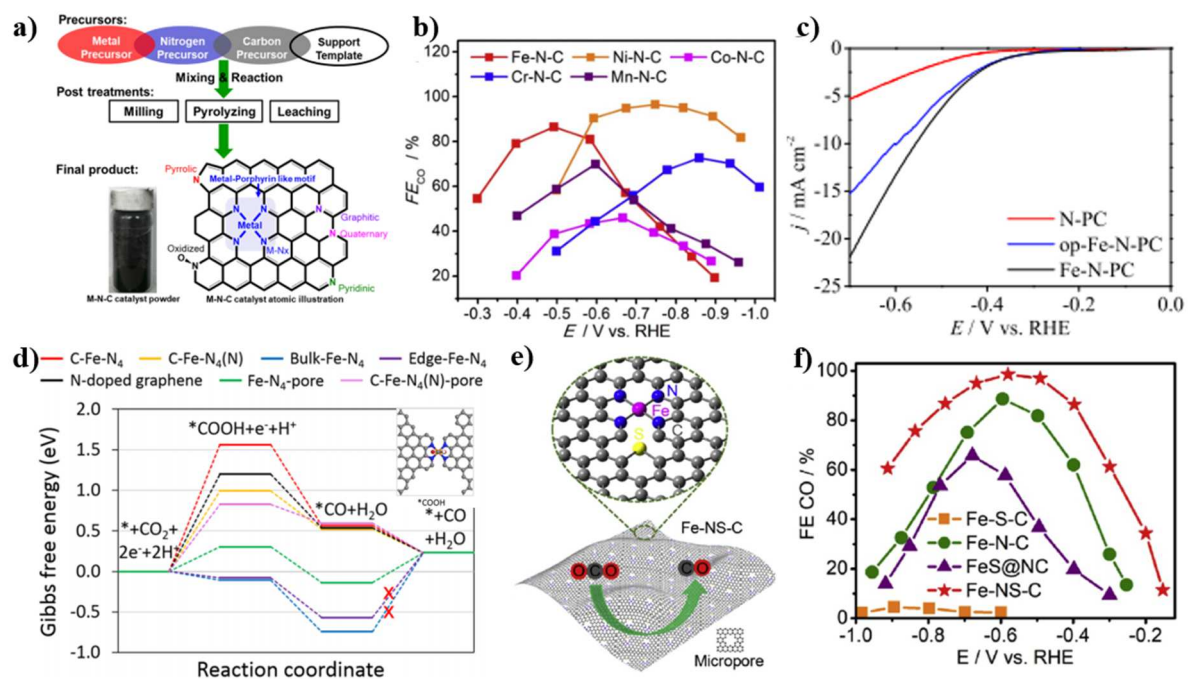
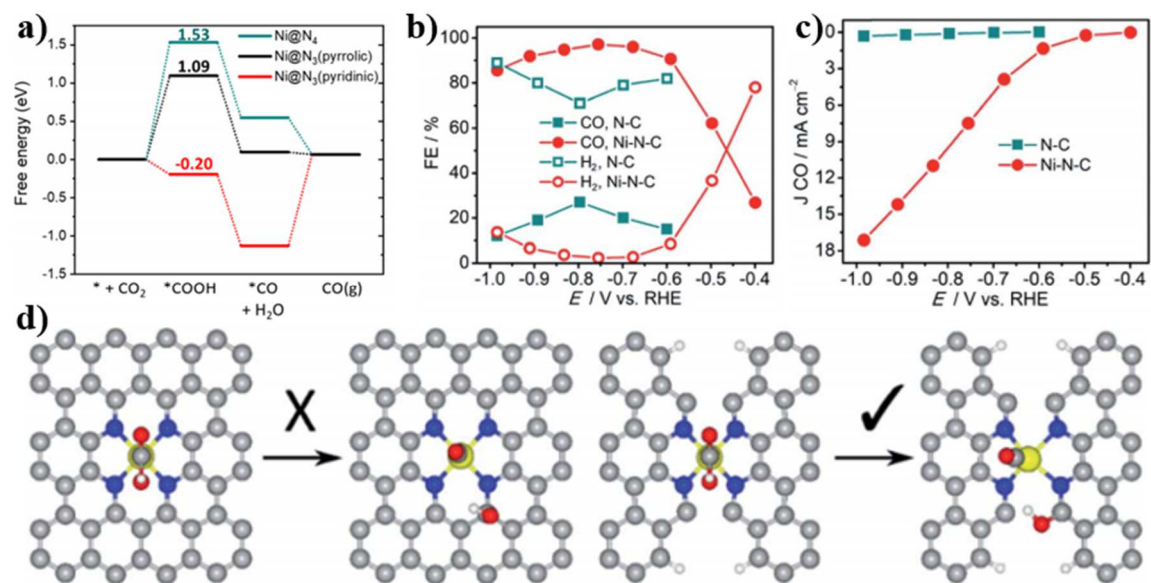


Fig.3.



## Appendix

Papers of particular interest, published within the period of review, have been highlighted as:

\* of special interest

\*\* of outstanding interest

*[5]	This review comprehensively summarized metal–organic complexes, metals, metal alloys, inorganic metal compounds and carbon-based metal-free nanomaterials for CO <sub>2</sub> reduction.
*[27]	Different abbreviation systems for denoting imidazolium-based room temperature ionic liquids (RTILs) used for CO <sub>2</sub> electrochemical conversion are reviewed about their physicochemical properties.
**[50]	This review analyzed various factors and described DFT directing experiments on the activity and selectivity of M-N-Cs.
**[60]	This paper strengthened the importance of single atoms Ni for CO <sub>2</sub> RR in several aspects and demonstrated different performance of various Ni active sites.
**[71]	This paper described cubic Cu <sub>2</sub> O crystalline particles electrochemically fragmentate into smaller particles and the grain boundaries generated can promote C-C coupling in CO <sub>2</sub> RR.
**[72]	This article demonstrated faster oxygen diffusion and oxide nucleation in Cu oxides catalyst for Cu reoxidation on grain boundaries.
**[74]	The authors illustrated products selectivity relies on surface roughness and revealed the effects of applied potential on the products selectivity of CO <sub>2</sub> RR.
**[80]	This paper showed an outstanding Faradaic efficiency (99%) for CO and studied the stable catalytic performance of the Fe-N-CSCN even with the addition of metal-ion impurities because of the numerous separated active sites.
*[81]	This paper proved the dopant sulfur in Fe-N-C structure can enhance the Faradaic efficiency to CO (98%).
**[86]	This paper adopted DFT calculation to compare the active sites of Ni-N <sub>4</sub> -C <sub>10</sub> and Ni-N <sub>2+2</sub> -C <sub>8</sub> and found that the edge-located Ni-N <sub>2+2</sub> -C <sub>8</sub> are responsible for the good performance of CO <sub>2</sub> RR because of lower free energy.